

# PHASE DIAGRAMS OF ELECTRIC-FIELD-INDUCED AGGREGATION IN CONDUCTING COLLOIDS.

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## 1. INTRODUCTION

Under the application of a sufficiently strong electric field, a suspension may undergo reversible phase transitions from a homogeneous random arrangement of particles into a variety of ordered aggregation patterns. The surprising fact about electric-field driven phase transitions is that the aggregation patterns, that are observed in very diverse systems of colloids, display a number of common structural features and modes of evolution thereby implying that a universal mechanism may exist to account for these phenomena. It is now generally believed that this mechanism emanates from the presence of the long-range anisotropic interactions between colloidal particles due to their polarization in an applied field. But, in spite of numerous applications of the electric-field-driven phenomena in biotechnology, separation, electrorheology, materials engineering, micro-devices for chemical analysis, etc. which have expanded rapidly over the last decade, our understanding of these phenomena is far from complete. Thus, it is the purpose of the proposed research to develop a theory and then test experimentally, under normal- and low-gravity conditions, the accuracy of the theoretical predictions regarding the effect of the synergism of the interparticle electric and hydrodynamic interactions on the phase diagram of a suspension.

The main results from our theoretical studies performed to-date enable one to trace how the variations of the electrical properties of the constituent materials influence the topology of the suspension phase diagram and then, by using an appropriate phase diagram, to evaluate how the electric-field-induced transformations will depend on the frequency and the strength of the applied field and the particle concentration.

## 2. ELECTRIC-FIELD-INDUCED PHASE TRANSITIONS

The first step in the development of a theory for the electric-field-induced phase transitions in a suspension of electrically uncharged conducting particles dispersed in a conducting fluid was taken in Refs. [1, 2]. To begin with, the density of the free energy of a suspension containing randomly arranged hard spheres subject to an electric field was written [1] as

$$F = k_B T f_0(c)/v_p - W \quad (1)$$

where the first term in Eq. (1) refers to the free energy of a suspension in the absence of the electric field, as a function of the temperature  $T$  with  $k_B$  being Boltzmann's constant, and the volume concentration of the particles  $c$  with  $v_p$  being the particle volume; the second term in Eq. (1) refers to the electric energy of a suspension caused by the interaction of the particles with the applied electric field and by the electric-field-induced long-range interparticle interactions. The concentration dependence of the function  $f_0(c)$  in Eq. (1) is well understood [3, 4].

The main obstacle which had to be overcome in constructing a theory of electric-field-induced phase transitions was that, for materials such as conducting suspensions whose complex dielectric permittivity  $\epsilon_s^* = \epsilon_s' - i\epsilon_s''$  varies strongly with the frequency of the applied electric field, the electric energy density  $W$  in Eq. (1) cannot be constructed using macroscopic electrodynamics [5]. The reason for this difficulty is that the frequency dependence of the dielectric permittivity implies that such a material contains mobile charges and electric dipoles capable of orientation, so that the stored electric energy will depend on the time-history of how the electric field was established [6].

To be sure, an expression for the electric energy density  $W$  of a conducting material, namely, Brillouin's formula (see Eq. (2) below), can be derived from macroscopic electrodynamics [5, 6], but only when the energy dissipation in this material is negligibly small and the time-variations of the applied electric field are very slow compared to the rate of relaxation phenomena, i.e.

$$W = \frac{1}{2} \frac{d}{d\omega} [\omega \epsilon_s'(\omega)] \langle E^2(\omega) \rangle_T \quad (2)$$

only if  $|\epsilon_s''(\omega)| \ll \epsilon_s'(\omega)$  and  $\omega t_s \ll 1$  where  $\omega$  and  $E(\omega)$  are the frequency and the Fourier amplitude of the applied electric field, respectively; the value of  $t_s$  determines the relaxation time of dielectric phenomena; and  $\langle \rangle_T$  denotes the time average.

Recall, that the real component  $\epsilon_s'$  gives the dielectric constant of a material whereas the imaginary

component  $\epsilon_s''$  determines the power dissipation (loss) in this material due to its conductivity. As can be seen from Eq. (2), Brillouin's formula is applicable only under the severe limitations that effects of conductivity are negligibly small so as not to cause losses in the stored electric energy. That is why Brillouin's formula cannot be utilized in Eq. (1) to describe electric-field-driven phase transformations in conducting colloids which strongly depend on conductivity effects.

To overcome the limitations of Brillouin's formula, we developed [1] a microscopic theory for the electric energy density  $W$  of conducting spheres dispersed in a conducting fluid when the particles were arranged randomly and provided that the particles and the suspending fluid can be described by the model of a leaky dielectric; i.e. when their dielectric constants,  $\epsilon_p$  and  $\epsilon_f$ , and conductivities,  $\sigma_p$  and  $\sigma_f$ , are frequency independent. This model corresponds to the classical mechanism of the so-called Maxwell-Wagner interfacial polarization typical of colloids [4, 7]. In this case, the short-term polarization of the particles and of the fluid is determined solely by their instantaneous polarization whereas their long-term polarization arises from the build-up of charge at the interface between the particles and the surrounding fluid. We exploited two microstructure-based techniques for solving the problem. One of them is based on a mean-field approximation (a cell model) where the average field acting on each particle is considered to be the well-known Lorentz-Lorenz local field [5, 6] rather than the applied field, while the second made use of statistical methods and a renormalization technique for calculating the  $O(c^2)$  term in the expansion for the electric energy density  $W$  in powers of the particle concentration. But, as we found [1], the main contribution to the electric energy of a suspension as well as to its complex permittivity is given by multiparticle interactions leading to a change in the local electric field acting on a particle. That is the reason why, for example, the cell model, which accounts only for this effect, yields the well-known Maxwell-Wagner expression for the complex

permittivity of a suspension which correlates well with experimental data.

The theory of Ref. [1] relates the electric energy density of a conducting suspension to the dielectric constants and conductivities of the particles and of the suspending fluid, the particle concentration, and the frequency and the strength of the applied electric field. To illustrate the advantages of this theory, the first two terms in the expansion of the electric energy density  $W$  in powers of the particle concentration were substituted in Eq. (1) which was then used to study the phase separation of a dilute conducting suspension subject to strong electric fields [1]. On this basis, we then calculated in Refs. [1, 2] the critical conditions beyond which the random arrangement of the particles becomes unstable in the presence of spatially uniform and non-uniform electric fields.

The main objective of the present work is to extend our previous studies [1, 2] beyond the dilute regime and to develop a microscopic theory for phase diagrams of concentrated conducting suspensions subject to strong dc and ac electric fields. To this end, we employ in Eq. (1) the full expression for the free energy density of a conducting suspension, as a function of a concentration, which we derived in Ref. [1] using the mean field approximation, and then investigate the topology of the suspension phase diagram, i.e. "the particle concentration-the electric field strength", and relate it to the electrical properties of the constituent materials.

As was shown in Ref. [1], the expression for the electric energy density  $W$  of a conducting suspension being subjected to a dc electric field  $E$  for short ( $t \ll t_s$ ) and for long ( $t \gg t_s$ ) times, is given by Eqs. (3) and (4), respectively, while, for an ac electric field  $E_0 \cos \omega t$  and for the long-term  $t \gg t_s$  regime, the equation for the time average of the electric energy of a suspension is given by Eq. (5)

$$W = \frac{\epsilon_f}{2} \frac{1 + 2c\beta_\epsilon}{1 - c\beta_\epsilon} E^2 \quad (3)$$

$$W = \left[ \frac{\epsilon_f}{2} \frac{1 + 2c\beta_\epsilon}{1 - c\beta_\epsilon} + \frac{9c(1-c)(\epsilon_f\sigma_p - \epsilon_p\sigma_f)^2}{2(\epsilon_p + 2\epsilon_f)(1 - c\beta_\epsilon)(\sigma_p + 2\sigma_f)^2(1 - c\beta_\sigma)^2} \right] E^2 \quad (4)$$

$$W = \left[ \frac{\epsilon_f}{4} \frac{1 + 2c\beta_\epsilon}{1 - c\beta_\epsilon} + \frac{9c(1-c)(\epsilon_f\sigma_p - \epsilon_p\sigma_f)^2}{4(1 + \omega^2 t_s^2)(\epsilon_p + 2\epsilon_f)(1 - c\beta_\epsilon)(\sigma_p + 2\sigma_f)^2(1 - c\beta_\sigma)^2} \right] E_0^2 \quad (5)$$

$$\text{with } t_s = \frac{(\epsilon_p + 2\epsilon_f)(1 - c\beta_\epsilon)}{(\sigma_p + 2\sigma_f)(1 - c\beta_\sigma)}, \quad \beta_\epsilon = \frac{\epsilon_p - \epsilon_f}{\epsilon_p + 2\epsilon_f}, \quad \beta_\sigma = \frac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f}.$$

For brevity, we included the vacuum permittivity  $\epsilon_0$  as a multiplier in the definition of dielectric constants  $\epsilon_p$  and  $\epsilon_f$  in Eqs. (4)-(5).

Equation (3) and the first terms in Eqs. (4) and (5), which are determined solely by the instantaneous polarization of the particles and the fluid, are consistent with the relationship for the electric energy of a non-

conducting suspension  $W = \frac{1}{2}\epsilon_s(c)E^2$  given by

macroscopic electrodynamics [5] with  $\epsilon_s(c)$  given by Maxwell's equation [7]. The second terms in Eqs. (4) and (5) correspond to the energy required to build the charge at the particle surface and to redistribute the electric field inside the particles and the suspending fluid when the time constants of the particles and of the fluid are different; that is when  $\epsilon_f/\sigma_f \neq \epsilon_p/\sigma_p$  [1]. But since the second term in Eq. (5) approaches zero as  $\omega t_s \rightarrow \infty$  the electric energy of the suspension for high frequencies becomes the same as that for a non-conducting material. On the other hand, for a slowly varying electric field,  $\omega t_s \ll 1$ , Eq. (5) yields the expression for the time average of the electric energy which is consistent with the expression given by the substitution of the Maxwell-Wagner relation for  $\epsilon'_s(\omega)$  into Brillouin's formula, Eq. (2), [1].

Now, the osmotic pressure of a suspension  $\Pi$  (equal to  $-(\partial F/\partial V)_{N,T,E}$  [8]) and the chemical potential of a particle  $\mu$  (equal to  $(F + \Pi V)/N$  [8]) can be evaluated from the equation of the free energy, Eq. (1). On calculating these expressions,  $f_0(c)$  is conveniently expressed in the terms of the suspension compressibility factor  $Z(c)$  where a good approximation for  $Z(c)$  of a suspension in the disordered state is given, for example [3, 4], by the Carnahan-Starling equation and the asymptotics  $Z \rightarrow \infty$  as  $c \rightarrow c_m$  where  $c_m \sim 0.63 - 0.64$  corresponds to random close packing of spheres.

The random arrangement of the particles in a suspension is stable as long as the osmotic pressure increases with concentration, which can be written as

$$\frac{\partial}{\partial c} \left( \frac{\Pi v_p}{k_B T} \right) = Z + c \frac{dZ}{dc} - c \frac{\partial^2}{\partial c^2} \left( \frac{W v_p}{k_B T} \right) > 0 \quad (6)$$

Consequently, as seen from Eq. (6), as long as the third term on the right-side is positive, in the other words as long as the interparticle interactions increase the suspension energy, an increase in the strength of the electric field decreases the value of  $\partial \Pi / \partial c$  and finally renders the random arrangement of the particles unstable when

$$\frac{\partial \Pi}{\partial c} = 0 \quad (7)$$

Now, Eq. (7) represents the spinodal curve in an equilibrium phase diagram of particle concentration vs. the electric field strength of a conducting suspension subject to an electric field. Specifically, this curve is the locus of points for which the curvature of the suspension free energy changes from convex to concave [8].

For the case when  $\partial^2 W / \partial c^2 > 0$  over the entire range  $0 \leq c < c_m$ , the spinodal points exist over the entire concentration range as well, so that increasing the strength of an electric field applied to this suspension will eventually cause the electric-field-induced transition. Thus, the phase diagram of such a suspension consists of the low-field one-phase region which includes the random spatial arrangement of the particles in the absence of an electric field and the high-field two-phase region corresponding to the appearance of aggregates caused by the action of an applied field. This phase diagram appears to be similar to the phase diagram concentration vs. temperature of a binary fluid or a binary alloy with a miscibility gap [8], so that these species exist in solution at high temperature but their mixture eventually separates into coexisting phases below the critical point of miscibility. In this regard, the application of an electric field to a conducting suspension is equivalent to a quench of an atomic system from its high-temperature one-phase state. Although such a similarity between the structural ordering in colloids and the structural behavior in conventional atomic systems- gas, liquid, crystal, and glasses- under suitable conditions has already been well recorded [3, 4], electric-field driven phase transitions in colloids have not been treated from this point of view thus far.

The critical point on the spinodal curve of the suspension, namely,  $c_{cr}$  and  $E_{cr}^2$ , coincides with the inflection point of  $\Pi$  as a function of  $c$ , so that Eq. (7) has a multiple root. In a two-phase region (at

$E^2 \geq E_{cr}^2$ ), the value of the osmotic pressure and of the chemical potential of the particles in the coexisting phases are equal. The latter leads to the following relations [8] between the particle concentrations in the both phases,  $c_1$  and  $c_2$ , respectively:

$$\mu(c_1) = \mu(c_2) \quad \text{and} \quad \Pi(c_1) = \Pi(c_2) \quad (8)$$

Now, Eqs. (8) represents the coexistence curve in the phase diagram of a suspension. This curve is located to the left of the spinodal curve in the low-concentration part of the phase diagram and to the right of the spinodal curve in the high-concentration part of this diagram. Moreover,  $c_1 \rightarrow c_{cr}$  and  $c_2 \rightarrow c_{cr}$  as  $E \rightarrow E_{cr}$ .

On the other hand, if the third term on the right-side of Eq. (6) is negative, in other words when the long-range interparticle interactions lower the suspension energy (i.e. when  $\partial^2 W / \partial c^2 < 0$  over the entire range  $0 \leq c < c_m$ ), an increase in the strength of the applied electric field increases the value of  $\partial \Pi / \partial c$ . In this case, the random arrangement of the particles appears to be stable, so that the phase diagram of such a suspension reduces to the one-phase domain.

As can be seen from Eqs (4)-(5), the sign of  $\partial^2 W / \partial c^2$  depends on the particle-to-fluid ratios of the conductivities and of the dielectric constants, the frequency of the applied electric field, and the particle concentration. For a high-frequency electric field when  $\omega t_s \rightarrow \infty$ , Eq. (5) yields

$$\frac{\partial^2 W}{\partial c^2} = \frac{3\epsilon_f \beta_e^2 E_0^2}{2(1 - \beta_e c)^3} > 0 \quad (9)$$

Thus, the sign of  $\partial^2 W / \partial c^2$  at  $\beta_e \neq 0$  always becomes positive over  $0 \leq c < c_m$  when the frequency of the applied electric field becomes sufficiently high. Hence it follows that there always exists a threshold value of the frequency, above which the particles having a dielectric constant different from that of the suspending fluid (regardless of the mismatch of their conductivities,  $\sigma_p / \sigma_f$ ) will aggregate as the strength of an applied electric field becomes sufficiently large. However, as we shall see, the sign of  $\partial^2 W / \partial c^2$  may become negative for low frequencies. If this happens over the entire concentration range,  $0 \leq c < c_m$ , the electric-field-induced aggregation of the particles will not occur at all. A peculiarity of concentrated suspensions is that the sign of the electric energy density of the interparticle interactions, i.e.

$\partial^2 W / \partial c^2$ , may change at some value of the concentration. As a result of this feature, which is absent in the theory for a dilute case [1], the ability or inability of the particles to aggregate in the presence of applied electric fields depends on the particle concentration as well.

As in the case of conventional atomic systems [8], the use of a spinodal curve provides a convenient way to distinguish "metastable" and "unstable" states of a suspension subject to an electric field, where we refer to the domain between the coexistence curve and the spinodal curve in its phase diagram as metastable, and the domain beyond the spinodal line as unstable. The free energy of a suspension, being considered as a function of the particle concentration, is convex in the metastable region of the phase diagram "the particle concentration-the electric field strength", so that the free energy will increase with a spontaneous concentration fluctuation, giving rise to an energetic barrier that will stabilize the suspension. The free energy, however, turns into a concave function of the particle concentration in the unstable region of the phase diagram, so that no energetic barrier to phase separation will exist in this state. This distinction can correspond to two different mechanisms of electric-field-induced transformations in a suspension: spinodal decomposition and nucleation, as occurs in atomic systems. For atomic systems, the former (in the unstable domain) corresponds to the growth of long-wavelength spontaneous concentration fluctuations with time whereas the nucleation of microdomains of the other phase starts the transformation for the latter (in the metastable domain). However, as recent research demonstrates (see review in Ref. [9]), there is no sharp dividing line between nucleation and spinodal transformations in atomic systems. Rather there exists a gradual transition in the dynamic behavior of a quenched system as the quench point on its phase diagram varies from one domain to the other in the vicinity of the spinodal curve.

In any event, we can expect that there exists some similarity between how spinodal and nucleation transformations operate in a suspension subject to an electric field and how they operate in quenched atomic systems, even though the electric-field-induced interparticle interactions are anisotropic. In this connection, we proceed in Sec. 3 to construct, based on Eqs. (7) and (8), a classification scheme which shall predict how the topology of the suspension phase diagram "the particle concentration-the electric field strength" depends on the particle and fluid dielectric constants and conductivities and the frequency of applied field. This will make it possible to exploit the great body of experimental data and theoretical

predictions available for the quenching of atomic systems and use it as a framework for interpreting the morphology and kinetics of aggregation patterns in colloidal suspensions generated by the application of electric fields.

### 3. CLASSIFICATION SCHEME OF DC- AND AC-FIELD PHASE DIAGRAMS

A thorough analysis of Eqs. (7) and (8) which yields a complete set of phase diagrams of suspensions subject to electric fields as a function of the mismatch of the dielectric constants and of conductivities of the particles to those of the fluid will be published elsewhere. Due to the limitations on the length of the paper, we consider only the main features of these diagrams shown in Fig. 1 where  $\lambda = \epsilon_r E^2 v_p / k_B T$  is the electric-to-thermal energy ratio, 1 and 2 are the spinodal and coexistence curves, and M and U denote the metastable and unstable domains.

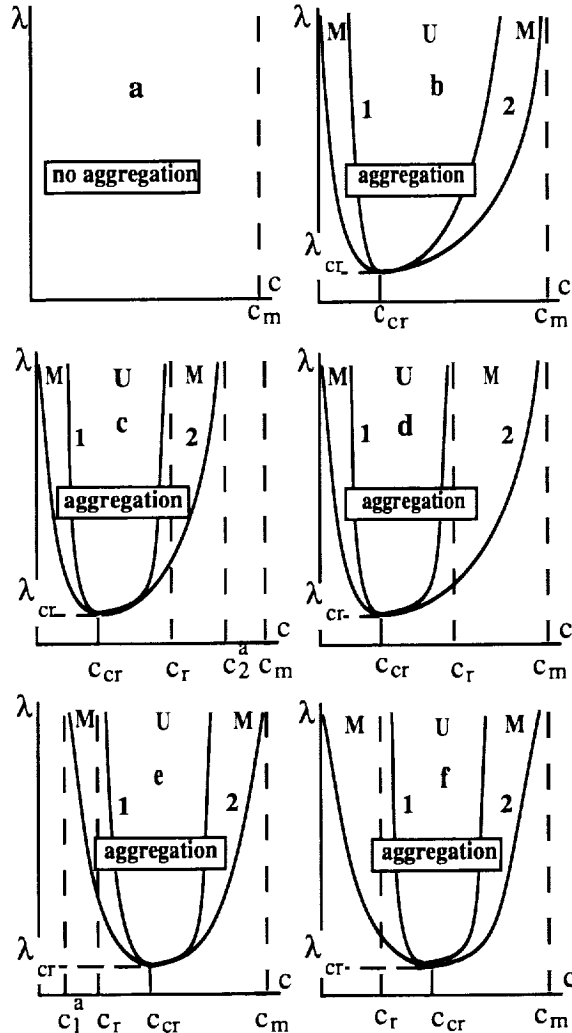


Figure 1.

The simplest phase diagram shown in Figs. 1a corresponds to the case when  $\partial^2 W / \partial c^2$  is negative over the entire concentration range,  $0 \leq c < c_m$ , so that no aggregation at all is predicted to occur in the presence of an electric field. In contrast, the phase diagram sketched in Figs. 1b shows the predicted behavior when  $\partial^2 W / \partial c^2$  is positive over  $0 \leq c < c_m$  so that, regardless of the particle concentration, the suspension will start aggregating as long as the applied dc field becomes sufficiently large.

The diagrams depicted in Figs. 1c and 1d are encountered when  $\partial^2 W / \partial c^2$  changes its sign with increasing concentration from positive at  $c=0$  to negative at  $c=c_m$ , so that it equals zero at some concentration  $c_r$ . The phase diagrams given in Figs. 1e and 1f represent the case when  $\partial^2 W / \partial c^2$  changes its sign with decreasing concentration from positive at  $c=c_m$  to negative at  $c=0$ , so that it equals zero at some concentration  $c_r$ . The separation between the spinodal and coexistence curves along the vertical lines of constant concentrations on the phase diagram in Fig. 1 increases indefinitely with increasing strength of the electric field.

As seen from Fig. 1, a metastable domain in the high-concentration parts of the phase diagrams in Fig. 1c (at  $c_r < c < c_2^a$ ) and Fig. 1d (at  $c_r < c < c_m$ ) as well as in the low-concentration parts of the phase diagrams in Fig. 1e (at  $c_1^a < c < c_r$ ) and in Fig. 1f (for  $0 < c < c_r$ ) is retained regardless of the strength of the applied dc field. Hence, only the nucleation mechanisms of electric-field-induced transformations will operate in such suspensions under these conditions. However, for the phase diagram in Fig. 1b, an increase in the electric field strength along the vertical line of constant concentration will inevitably lead to the transition from a metastable to an unstable domain at any concentration. Thus for such suspensions, the nucleation mechanism will operate in weak fields (below the spinodal curve) whereas the spinodal decomposition will inevitably operate in strong fields (above the spinodal curve). This qualitative distinction between the transformation mechanisms should manifest itself by the dependence of the morphology of the aggregation patterns to be formed on the strength of the applied field.

The map plotted in Fig. 2 demonstrates how the topology of the phase diagram of a suspension subject to dc fields relates to the mismatch of the dielectric constants and the conductivities of the particles and

those of the suspending fluid. The domains in Fig. 2 are lettered to correspond to the phase diagrams in Fig. 1 whereas the numbers 1, 2, 3, and 4 denote the curves

$$\partial^2 W / \partial c^2 \Big|_{c=c_m} = 0, \quad \partial^2 W / \partial c^2 \Big|_{c=0} = 0,$$

$$\int_0^{c_m} c (\partial^2 W / \partial c^2) dc = 0, \text{ and}$$

$$\int_0^{c_m} (c_m - c) (\partial^2 W / \partial c^2) dc = 0, \text{ respectively.}$$

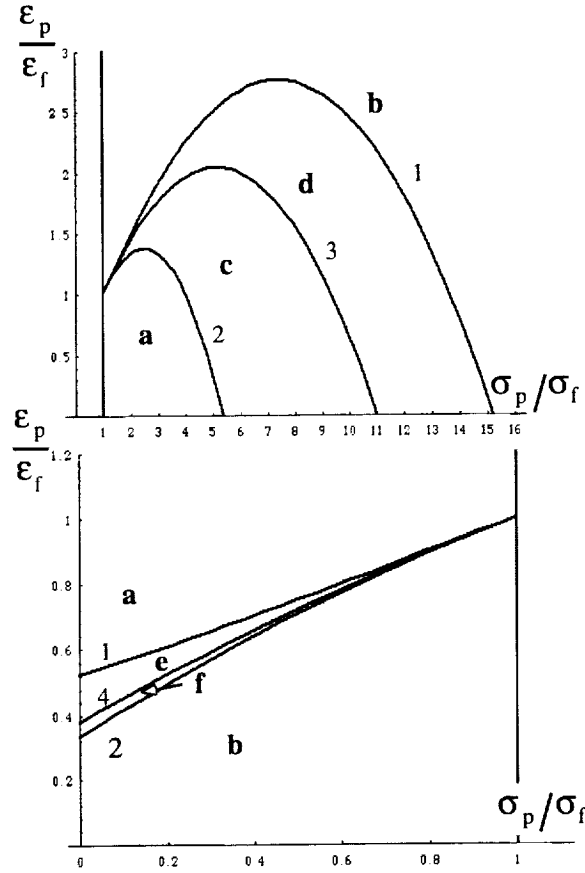


Figure 2.

An increase in the frequency of an ac electric field affects the shape and the size of sub-domains in Fig. 2. For example, as  $\omega t_s$  increases, the domain "a" located in the region  $\sigma_p < \sigma_f$  shrinks to the line  $\epsilon_p = \epsilon_f$ , so that it disappears gradually as  $\omega t_s \rightarrow \infty$ . On the other hand, the domain "a" located in the region  $\sigma_p > \sigma_f$  is retained while its boundaries move indefinitely to the right as  $\omega t_s \rightarrow \infty$  and, moreover, the separation between them along the lines  $\epsilon_p / \epsilon_f = \text{const}$  increases. In particular, this

demonstrates why  $\partial^2 W / \partial c^2$  should always become positive at any fixed values of the  $\sigma_p / \sigma_f$  and  $\epsilon_p / \epsilon_f$  ratios as the field frequency is made sufficiently high.

It should be pointed out that the particle content,  $c_2$ , of the high-concentration phase of a suspension in the phase diagrams in Fig. 1 increases dramatically with the strength of the applied field. Thus, it is quite realistic to suppose that a high-concentration phase in the diagrams in Fig. 1 should undergo subsequent disorder-to-order transitions in the presence of sufficiently strong electric fields as occurs in the absence of an electric field [3, 4]. In this connection, we also mention recent studies of non-conducting suspensions subject to strong electric fields [10] which demonstrate that a high-concentrated phase in such colloids eventually form a crystalline body-centered tetragonal solid. Unfortunately, a description of these transformations cannot be included in the diagrams in Fig. 1 because of the absence of an equation for the free energy of conducting anisotropic aggregates, which is required for this analysis.

#### 4. ACKNOWLEDGEMENT

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